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POTASSIUM HYDROXIDE MODIFICATION AND CHARACTERIZATION OF NANO-ZINC OXIDE IN METHANOLYSIS OF RICE BRAN OIL

KAMALUDDEEN SULEIMAN KABO

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requirements for the award of the degree of
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Dedicated to

My mother, Rabi'atu Nuhu Imam, for her unlimited sacrifice:
My father, Alhaji Suleiman Ahmad Kabo, for his unlimited support:
My wife, Asiya Muhamad Yahaya, for her unrelenting support and understanding
And
My children Ahmad, Khadija and Aisha, source of my constant joy and inspiration.
All of which help during my pursuit to acquire the doctoral degree

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ABSTRACT

Biodiesel is an alternative biofuel that could help to reduce the use of fossil fuels and protect the environment. However, its production is still challenged by catalyst development, evaluation and process optimization. In this research, new structure and base modified zinc oxide nanocatalysts were prepared and used in the methanolysis of rice bran oil (RBO). The catalysts were characterized by field emission scanning microscope (FESEM), powder X-ray diffraction (XRD), nitrogen adsorption, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF) and basic concentration back titration analyses. While, biodiesel was characterized by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and gas chromatography flame ionisation detector GC-FID method. The results showed that different nanoparticles were successfully prepared from direct precipitation; nanoflowers and nanotubes attained through hydrothermal methods without the use of any surfactant or templating agent. The synthesized nanostructures were base-modified using KOH by wet impregnation using Response Surface Methodology-Box Behnken Design (RSM-BBD) method. It was observed that nanoparticles and nanotubes have the lowest crystallite sizes of 34.32 and 29.96 nm, are mesoporous in nature, having open ended tubular pores with BET surface areas of 12.82 and 14.29 m^2g^{-1}, pore sizes of 46.93 and 42.57 nm and pore volumes of 0.1315 and 0.1475 cm^3g^{-1}, respectively. The XRD, nitrogen adsorption and FTIR analyses showed the presence of K as substituent in ZnO lattices after modification, which was confirmed by XPS with proposed molecular formula as $Zn_{(1-x)}K_xO$ and supported by XRF indicating the atomic weight percentage as 2.24%. Although both structure and base modification affect the basic sites concentration, but base modification has more influence, the K-modified ZnO nanotubes having the highest basic sites of 8.82 mmol/g. The RSM was used for the methanolysis experimental design and optimization. Analysis of biodiesel products shows the highest biodiesel yield of 96.24% in 90 min was observed from K-modified nanotubes, followed by nanoparticles, 95.95% in 120 min and nanoflower 94.82% in 120 min. Catalyst loading of 3.7%, methanol to oil ratio 1:9 and temperature of 65°C was used as the optimum conditions. Results from catalyst reusability and leaching tests show that among the nanostructures, K-modified nanotubes undergo minimum leaching and the highest recyclability. Thus, structure modification using simple growth and impregnation methods helped in the preparation of efficient basic transesterification catalysts, such that the nanotubes are the best catalysts, which demonstrated high biodiesel yield and stability for use at relatively lower reaction conditions.

ABSTRAK

Biodiesel adalah bahan api bio alternatif yang boleh membantu untuk mengurangkan penggunaan bahan api fosil dan melindungi alam sekitar. Walau bagaimanapun, pengeluarannya masih tercabar oleh pembangunan mangkin, penilaian dan pengoptimuman proses. Dalam penyelidikan ini, struktur baru dan nanomangkin zink oksida terubahsuai bes telah disediakan dan digunakan dalam metanolisis minyak bran beras (RBO). Mangkin telah dicirikan oleh mikroskop pengimbasan elektron pemancaran medan (FESEM), pembelauan sinar-X serbuk (XRD), penjerapan nitrogen, spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi fotoelektron sinar-X (XPS), pendarfluor sinar-X (XRF) dan analisis pentitratan balik kepekatan bes. Manakala, biodiesel dicirikan menggunakan kaedah proton resonans magnet nukleus (^{1}H NMR) dan kromatogafi gas pengesan pengionan nyalaan (GC-FID). Keputusan menunjukkan nanopartikel yang berbeza telah berjaya disediakan daripada pemendakan langsung; nanobunga dan nanotiub telah didapati melalui kaedah hidroterma tanpa menggunakan sebarang surfaktan atau ejen penemplatan. Nanostruktur yang disintesis telah diubah suai dengan bes menggunakan KOH secara pengisitepuan basah menggunakan kaedah gerak balas permukaan-reka bentuk Box-Behnken (RSM-BBD). Diperhatikan bahawa nanopartikel dan nanotiub mempunyai saiz kristalit terendah iaitu 34.32 dan 29.96 nm, adalah bersifat mesoliang, mempunyai liang tiub hujung terbuka dengan luas permukaan BET 14.29 dan 12.83 m^2g^{-1}, saiz liang 46.93 dan 42.57 nm dan isipadu liang 0.1475 dan 0.1315 cm^3g^{-1}, masing-masing. Analisis XRD, penjerapan nitrogen dan FTIR menunjukkan kehadiran K sebagai bahan penukar ganti dalam kekisi ZnO selepas pengubahsuaian, yang telah disahkan oleh XPS dengan formula molekul dicadangkan sebagai $Zn_{(1-x)}K_xO$ dan disokong oleh XRF yang menunjukkan peratusan berat atom sebagai 2.24%. Walaupun kedua-dua struktur dan pengubahsuaian mempengaruhi kepekatan tapak bes, namun K-terubahsuai nanotiub ZnO mempunyai tapak bes tertinggi iaitu 8.82 mmol g^{-1}. RSM telah digunakan untuk mereka bentuk eksperimen metanolisis dan pengoptimuman. Analisis produk biodiesel menunjukkan hasil biodiesel tertinggi yang diperoleh ialah 96.24% dalam masa 90 min, dicerap bagi nanotiub K-terubahsuai diikuti oleh nanopartikel, 95.95% dalam masa 120 min dan nanobunga, 94.82% dalam masa 120 min. Muatan mangkin sebanyak 3.7%, nisbah metanol kepada minyak 1:9 dan suhu 65^{o}C telah digunakan sebagai keadaan optimum. Keputusan daripada ujian guna semula mangkin dan larut lesap menunjukkan bahawa di kalangan nanostruktur, nanotiub K-terubahsuai mengalami larut lesap minimum dan boleh dikitar semula paling tinggi. Oleh itu, pengubahsuaian struktur menggunakan pertumbuhan mudah dan pengisitepuan membantu dalam penyediaan mangkin transesterifikasi berbes, sehinggakan nanotiub adalah yang terbaik, dengan menunjukkan hasil biodiesel yang tinggi dan kestabilan untuk digunakan pada keadaan tindak balas yang relatif lebih rendah.

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LIST OF ABBREVIATIONS

^{1}HNMR	-	Proton Nuclear Magnetic Resonance
ANOVA	-	Analysis of Variance
AR	-	Analytical Reagent
ASTM	-	American Standard for Testing of Materials
BBD	-	Box Behnken Design
BET	-	Branneur-Emmet-Teller
BJH	-	Barrett–Joiner–Halender
CNT	-	Carbon nanotubes
DF	-	Degree of Freedom
DG	-	Diglyceride
DOE	-	Design of Experiment
FAME	-	Fatty Acid Methyl Ester
FESEM	-	Field Emission Scanning Electron Microscopy
FID	-	Flame Ionization Detector
FFA	-	Free Fatty Acid
FT	-	Fischer−Tropsch
FTIR	-	Fourier Transform Infrared
FWHM	-	Full Width at Half Maximum
GC	-	Gas Chromatography
GL	-	Glycerol
HVO	-	Hydro-treated Vegetable Oil
HPLC	-	High Performance Liquid Chromatography
ICP	-	Inductively Coupled Plasma
IR	-	Infrared
MG	-	Monoglyceride
MOR	-	Methanol to Oil Ratio

MSDS	-	Material Safety and Data Sheet
NA	-	Nitrogen Adsorption
NF	-	Nanoflowers
NFK	-	Nanoflowers Potassium-modified
NMR	-	Nuclear Magnetic Resonance
NP	-	Nanoparticles
NPK	-	Nanoparticles Potassium-modified
NT	-	Nanotubes
NTK	-	Nanotubes Potassium-modified
RMM	-	Relative molecular mass
SEM	-	Scanning Electron Microscopy
SS	-	Sum of Squares
STP	-	Standard Temperature and Pressure
TAG	-	Triacyl Glycerides
TG	-	Triglyceride
XRF	-	X-Ray Fluorescence
XPS	-	X-Ray Photoelectron Spectroscopy
XRD	-	X-Ray Diffraction
WCO	-	Waste-Cooking Oil
RBO	-	Rice Bran Oil
RSM	-	Response Surface Methodology
TOF	-	Turnover Frequency

LIST OF SYMBOLS

$\delta+$	-	Partial negative charge
$\delta-$	-	Partial positive charge
^{o}	-	Degree
%	-	Percent
µ	-	Micro
β	-	Full width at half maximum
β_{o}	-	Intercept
β_{i}	-	First order coefficient of the model
β_{ii}	-	Quadratic coefficient of the model
β_{ij}	-	Linear coefficient of the model
θ	-	Angle of measurement
γ	-	Magnetogyric ratio
l	-	Spin quantum number
ϕ	-	Parameter, depends on XPS spectrometer and the sample
λ	-	Wavelength of radiation
$\mathcal{E}$	-	Experimental error
$\sum$	-	Summation
ΔG	-	Gibb's free energy
ΔH	-	Enthalpy change
ΔS	-	Entropy change
a	-	Lattice parameter
A	-	Pre-exponential factor
A_1	-	Area of methoxy protons from methyl esters
A_2	-	Area of methylene proton from the esters
d	-	Distance between the scattering planes
Ea	-	Activation

E_B	-	Binding energy of specific core or valence level electron
E_k	-	Photoelectric kinetic energy of valence electron
f_w	-	Catalyst's active sites
h	-	Plank's constant
hv	-	Characteristic photon energy of the excitation source
k	-	Rate constant
k_B	-	Boltzmann's constant
K	-	Constant ≈ 1
L	-	Average crystallite size
M	-	Molar mass
m_{cat}	-	Mass of catalysts
n	-	order of the reflection
P	-	Adsorption equilibrium pressure
P_o	-	Standard vapour pressure of the adsorbate
pH	-	Degree of acidity or alkalinity
R	-	Universal gas constant
T	-	Temperature
w	-	Weight
χ		Constant related to heat of adsorption of an adsorbate
x	-	Concentration
X_1	-	First factor
X_2	-	Second factor
X_3	-	Third factor
X_4	-	Fourth factor
Y	-	Response factor
V_o	-	Volume of adsorbate required for monolayer coverage
V_a	-	Volume at STP of the molecules adsorbed

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

In recent years, the development of alternative fuels, like bioethanol, biodiesel and biokerosene from renewable resources, has received considerable attention. Worldwide energy demand, particularly for liquid transportation fuels, continues to rise as populations grow and become more affluent. Continued use of fossil fuels is generating concern because of the large amounts of carbon dioxide released into the atmosphere which results in more greenhouse emission leading to increased risk and adverse effects of global warming. In view of this, renewable sources of energy are required for sustainable development of modern society but there is challenge of properly exploiting their potential for applications compared with the traditional energy sources. In order to reduce the production and effects of greenhouse gas emissions, alternative fuels especially biofuels with optimum properties seem to be a promising solution.

Fuels produced from renewable resources, such as wood biomass, sugars, and vegetable oils, are attracting growing interest because they fit into carbon cycle, their effect on the atmosphere is more carbon-neutral and they are less toxic in the environment. Plant biomass is the main source of renewable materials on Earth and represents a potential source of renewable energy and bio-based products. The substitution of fossil fuels by biomass is an important contribution to reduce anthropogenic net CO_2 emissions. Biomass is available in high amounts as forest, agricultural or industrial wastes, lignocellulosic and crops at relatively low cost, it could be a widely available and inexpensive source for biofuels and bio products in the near future (del Río *et al.*, 2012). Biofuels are mixtures of renewable molecules such as normal and iso-paraffins, synthetized using industrial processes like Fischer−Tropsch (FT) and Hydro-treatment of Vegetable Oils (HVO), naphthenic and aromatic compounds obtained from the liquefaction or the pyrolysis of biomass. They also include alcohols from fermentation processes and esters using transesterification processes from raw vegetable oils such as rapeseed, sunflower, palm, or jatropha (Saldana *et al.*, 2012). Bioethanol, biodiesel, biokerosene, biogas, biomass, and bio-oils are the most attractive alternatives for replacing rapidly depleting and increasingly expensive petrofuels. They are currently being investigated to optimize their production to be used competitively as replacements for liquid petroleum fuels. This can help to address concerns over environmental pollution and climate change caused by excessive usage of petroleum fuels and serve as alternative to declining petroleum reserves.

However, technologies are needed for biomass yield processes which are able to economically transform all the energy in the diverse biomass sources to a transportation fuel that may be used without major modification to engines (Garcia-perez, *et al.*, 2007). The production of fuels from biomass requires the development of new chemical pathways to convert the oxygenated renewable feedstock into molecules with the appropriate molecular weight and structure for use as liquid fuels (Gaertner, *et al.*, 2010). Though bioethanol can be obtained from a variety of cheap raw-materials, but it can only be used in mixed form with petrol. However, biodiesel when produced in good quality can be used both in mixed and pure form on the current diesel engines. Production of biodiesel is easy, but the major challenges with biodiesel remain with availability of cheap raw materials and optimization of catalyst for better activity in order to make the process commercially viable.

Many works on homogeneous and heterogeneous biodiesel production processes were reported. However, heterogeneous catalysts are prepared due to problems associated with homogeneous catalysts which their use as catalysts causes environmental damages and high cost of biodiesel. Heterogeneous basic catalysts where found to be better compared to heterogeneous acid catalysts in biodiesel production, though they show better tolerance to the presence of high FFA in oils. Metal oxides are mostly used because of their ability to supply positive metal ions which will attract the alcohol molecule to form metallic alkoxide that would attack the triglyceride oil molecules, leading to its final yield to ester or biodiesel. But most of them have low activity or deactivate easily which necessitate the use of various modification processes to improve their performance. Modifications could be achieved through doping, coprecipitation or structural modification, all with aim of exposing catalyst active sites for better performance. Presently, emphasis is given to the use of environmentally benign catalysts to mitigate the negative effect associated with the use of many other catalysts in biodiesel production.

Zinc oxide bio-safe with very low toxicity levels and ability to be produced in a variety of structures (Wang, 2004), it is highly insoluble, does not easily leach, is recyclable (Yan *et al.*, 2010), abundant, cheap and contains both Lewis acid and base active sites, making it attractive in catalytic applications (Molina, 2013). These are good properties needed in heterogeneous catalyst as there is less danger of pollution and enable ease of phase separation after product formation. Thus, zinc oxide could be modified to serve as heterogeneous catalyst in biodiesel production. Morphological modification could expose polar sites and reduce excessive use of active substances in the acid or basic modification. This can help to optimize the modification process and improve the performance and stablity of catalysts

For the production of biodiesel at lower cost in order to compete with price of mineral diesel at market, lower reaction conditions have to be used. A temperature not higher than 65 ^{o}C: the boiling point of methanol is prepared as it can enable biodiesel production at atmospheric conditions without considerable loss of methanol or complex instrumentation. Other factors especially time when optimized can help to save energy and lower the production cost.

Rice bran oil (RBO) is a feedstocks obtainable from the agricultural wastes of food production like when used as energy source can provide twin advantages. Their use will cause improve on the economic value of the plant, increase food production and serve as sustainable alternative energy source. This can address the issue raised by the critics of biofuels which highlighted the consquence of the use of food sources in fuel production. Other sustainable feedstocks with lower the cost for competitive price are also considered; non-refined, waste cooking, non-edible and algae oils could be used. But mostly, they have high frre fatty acid (FFA) content and can easily form soap and deactivate catalysts. Though two step reactions involving esterification with acid followed by transesterification with base could be used, but it is slow, time and energy consuming.

1.2 Statement of the Problem

There are general or traditional problems associated with exploration, processing and use of fossil fuels, the most serious being the global warming (Serrano-ruiz and Ramos-fern 2012) due to increasing emission of greenhouse gases as a result of road transportation, aviation and industrial activities, others include oil spillage, price hike and scarcity. The use of homogeneous catalysts in transesterification to produce biodiesel leads to many problems such as non-recyclability, contamination with metal ions due to leaching, release of large quantity of water from washing to purify biodiesel which contains high concentration of organic contaminants, formation of soap during transesterification, leading to reduced catalytic activity and difficulty in the product separation and purification.

Zinc oxide alone has low activity in transesterification reaction and so its use always require elevated reaction parameters like temperatures above 150^{o}C (Nambo *et al.*, 2015) or supercritical conditions (Kim *et al.*, 2013) which also add cost to the production. In order to use ZnO in lower conditions and achieve good oil to ester yield its properties have to be modified.

The use of large amount of active substances in modification lead to instability, causing leaching and reduced activity. But different structures and morphology of solid catalysts play important roles in heterogeneous applications like photocatalysis and transesterification (Li and Haneda, 2003; Joon *et al.*, 2006; Yu and Yu, 2008;

Sathishkumar *et al.*, 2011; Garces *et al.*, 2012; Nambo *et al.*, 2015). This is largely due the exposure of polar axis during the development of stuctures which can lead to increased activity of catalysts. The use of nanoparticles ZnO (Yan *et al.*, 2008) and nanorods ZnO (Nambo *et al.*, 2015) in biodiesel production were reported but under higher reaction temperatures. However, the use of other nanostructures particularly nanoflowers and nanotubes in transesterification has not been reported in the literature.

The use of higher reaction temperatures, problems of recyclability or leaching associated with those catalysts.The use of higher temperature above 65 ^{o}C , the boiling point of methanol need added preparation to prevent its escape. This, together with increased energy consumption at higher temperature raises the production costs of biodiesel Thus, in order to obtain biodiesel at lower price to compete with mineral diesel, lower temperature, preparably not higher than 65 ^{o}C together with time not higher than 3 hrs should be used.

KOH alone is very good homogeneous catalyst with excellent yield in transesterification reactions for biodiesel. But there are so many problems of phase, catalyst and glycerol separation associated with homogeneous catalysts and so have to be avoided. The use KOH supported on some substances for heterogeneous application in biodiesel was also investigated and it was reported to show remarkable improvement on their catalytic activity. KOH-MgO (Ilgen and Akin, 2009) K-CaO (Kumar and Ali, 2012) KOH/Zeolite (Jo *et al.*, 2012) KOH-alumina (Ghasemi and Dehkordi, 2014), KOH/Zirconia (Takase *et al.*, 2014) were all reported to be used in transesterification with various degree of yield. However, despite the advantages of using zinc oxide as heterogeneous catalyst, information from the available literature shows no detailed work was carried out on the modification of zinc oxide with KOH for the transesterification. In particular, the use of KOH-modified zinc oxide in transesterification of rice bran oil has not been reported. Also, full evaluation of recyclability, kinetics and thermodynamics of these catalysts was not available in the literature.

Rice bran oil is obtained from rice bran, most of which is considered as agricultural waste in paddy farms. This is especially in Africa and particularly in northern Nigeria even though rice is produced in large quantities but greatly under-utilized. Though, some critiques highlight the use of vegetable oils for biodiesel production can cause food versus fuel competition which may result in significant increase in the cost or food shortage (Khan *et al.*, 2014). But rice being one of the major global staple foods is produced in large quantities, the use of previously wasted rice bran to extract oil for biodiesel production will actually increase the value of rice. Hence, encouraging its production which will help to improve local economies, increase food production and serve as alternative energy source.

1.3 Research Hypothesis

It is expected that catalytic activity of zinc oxide will be influenced by structural modification due to morphological differences associated with nanoparticles, nanoflowers and nanotubes. The use of response surface methodology (RSM) optimization on the modification will help to prepare high basic sites K-modified ZnO with minimum amount of KOH will produce an active catalyst for the production of biodiesel production. Biodiesel would be obtained at lower reaction conditions from the prepared catalysts. Both structural and base modification of zinc oxide will have significant effect on the catalyst activity; biodiesel yield and catalyst stability; reusability and leaching. Both structural and basic modification will have significant effect on the kinetics and thermodynamics parameters of the transesterification process.

1.4 Objectives of the Research

The following are the objectives of this research work.

1. To prepare various type of ZnO structures, beginning with commercial ZnO, followed by preparation of synthetic nanostructures; nanoparticles, nanoflowers and nanotubes form zinc oxide acetate precursors.

2. To prepare base modified ZnO catalysts using potassium hydroxide through wet impregnation method with aid of RSM optimization to obtain optimum modification parameters (KOH-loading, calcination temperature and calcination time).

3. To carry out characterization of the catalysts and determine their active sites before and after K-modification in order to access the effect of morphology and base modification on basic sites

4. To prepare biodiesel at lower reaction conditions (65 ^{o}C or below, 3 hrs or below) using the structure and base modified zinc oxide samples as catalysts, optimize the production process with RSM design and determine the catalysts stability by carrying out leaching and recyclability tests.

1.5 Scope of the Research

The scope this research covered the development, characterization, use and evaluation of structural and base modified ZnO nanostructures for use as stable catalysts in biodiesel production.

The first stage was the preparation of different ZnO structures. Starting with preparation of surface modified commercial ZnO through hydration-dehydration technique which include reflux with water followed by calcination. Then, preparation of nanoparticles, nanoflowers and nanotubes ZnO nanostructures by precipitation and hydrothermal methods. After that, surface modified commercial ZnO was base modified with KOH by wet impregnation under RSM optimization with "Design Expert 7.1.6" statistical software. Optimized modification parameters obtained would be adopted and applied for base modification of synthesized ZnO nanostructures. These catalysts would be characterized by field emission scanning electron microscopy (FESEM), X-Ray powder Diffraction (XRD), nitrogen adsorption Brunauer-Emmet-Teller (BET) and Barrett-Joiner-Halender (BJH) surface analysis, Fourier transform Infra-red (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF) and basic sites back titration analysis techniques.

After preparation and characterization, the catalysts were used to produce biodiesel through batch transesterification reaction of rice bran oil (RBO) with methanol. Also, the methanolysis reaction with commercial ZnO would be optimized using RSM design of experiment with aid “Design Expert 7.1.6” statistical software. Optimized parameters (catalyst loading, reaction temperature, time and methanol to oil ratio (MOR)) obtained from commercial were adopted and applied in the methanolysis with the synthesized nanostructures. gas chromatoraphy flame ionisation detector (GC-FID) and proton nuclear magnetic resonance (^{1}H NMR) techniques were used in the analysis of the products. Recyclability of the catalysts and leaching were also evaluated.

1.6 Significance of the Research

Biodiesel prepared can be used as alternative energy source for application in industrial, agriculture and transportation sectors which can help to reduce the problem global warming associated with the use of fossil fuels. The research prepared new structure and base modified zinc oxide based catalysts with readily available raw materials through simple impregnation, hydrothermal and coprecipitation methods for biodiesel production.

The use of zinc oxide as catalyst will help to address the problem of catalyst toxicity, leaching.

The use of nanostructured materials in biodiesel production will help reduce excessive use of active substance in modification and improve catalysts performance and stability.

Lower reaction conditions will reduce the cost and enhance the sustainability of biodiesel production.

Recycling of the catalyst due to reduced leaching will help in biodiesel commercialization, reduce production cost environmental pollution.

The use of greatly under-utilized rice bran oil will help to reduce the agricultural waste and problems associated with its burning and improve the economic value of the crop especially in Africa and other developing nations.

RSM study will help to reduce the cost and time in catalyst modification and biodiesel production, optimization and analysis.

1.7 Thesis Structure

In general, the thesis is presented in seven chapters based on the flow of research activities, experimental works, discussion of findings and conclusion

Chapter 1 presents the general background of the area of interest, problem statement, hypothesis, objectives of the research, scope of the research, significance of the research and explanation of the thesis structure.

Chapter 2 presents a comprehensive review of related literature survey. Information on the prospect of renewable energy, especially as related to the use of heterogeneous catalysts for biodiesel. The effect of base and nanostructures and in particular ZnO for the use in biodiesel production were all presented.

Chapter three presents the methodology used in the catalysts preparation, modification, optimization and characterization. It contains methodology on biodiesel production, optimization and characterization.

Chapter four presents results and discussion on the catalysts preparation, modification, optimization and characterization.

Chapter five presents results and discussion on biodiesel production, optimization and characterization.

Chapter six provides summary, conclusions and recommendations for further works in this area.

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